

<b>TITLE:</b>	<b>THE HOMOGENEOUS FORCING OF MERCURY OXIDATION TO PROVIDE LOW-COST CAPTURE</b>
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<b>GRANT NO.:</b>	DE-FG26-03NT41808
<b>PERIOD OF PERFORMANCE:</b>	July 2003 - June 2006

## OBJECTIVES

Combustor-generated oxidized mercury (*e.g.*, HgCl<sub>2</sub>) is known to be much more easily captured in existing pollution control equipment (*e.g.*, wet scrubbers for SO<sub>2</sub>) than elemental mercury. This is principally due to the high solubility of the oxidized form in water. Work over the last several years in our lab and elsewhere has identified the general outlines of the homogeneous chemistry of oxidation.

The scenario is as follows. In the flame the mercury is quantitatively vaporized as elemental mercury. Also, the chlorine in the fuel is released as HCl. In the high temperature flame, a small fraction of the HCl decomposes to give atomic chlorine. As the gases cool, the recombination of this atomic chlorine to Cl<sub>2</sub> is kinetically inhibited, leading to a superequilibrium excess of Cl in the postflame region. Once the gases drop below about 800 K, the mercury equilibrium shifts to favor HgCl<sub>2</sub> over Hg, and this superequilibrium chlorine atom promotes oxidation via the fast reactions  $\text{Hg} + \text{Cl} + \text{M} \rightarrow \text{HgCl} + \text{M}$  and  $\text{HgCl} + \text{Cl}_2 \rightarrow \text{HgCl}_2 + \text{Cl}$ . Thus, the high temperature region provides the Cl needed for the reaction, while the quench region allows the Cl to persist and oxidize the mercury in the absence of decomposition reactions that would destroy the HgCl<sub>2</sub>. The next question is how to make use of the knowledge to *promote* oxidation. The hypothesis is that introduction of fuel species (specifically H<sub>2</sub> or CO) in the post flame gases leads to an enhancement in atomic chlorine concentrations, resulting in increased fractional mercury oxidation. Chemical kinetic modeling suggests that this occurs due to the free radicals generated by the decomposition of the fuel. This leads to reactions such as:  $\text{OH} + \text{HCl} \rightarrow \text{Cl} + \text{H}_2\text{O}$ . The present grant focuses on exploring and optimizing this hypothesis.

## ACCOMPLISHMENTS TO DATE

The experiments are conducted in a quartz plug flow reactor system. The reactants are preheated separately and mixed in a system that allows an approximately 0.5 second residence time at a selected constant temperature. The gases are then quenched to room temperature in a well-characterized quench zone before the mercury oxidation state is measured by cold vapor atomic absorption. The species present under the baseline conditions include O<sub>2</sub> (10%), H<sub>2</sub>O (5%), HCl (varying between 0-300 ppm), Hg (900 µg/m<sup>3</sup>), balance N<sub>2</sub>. Using this system we have systematically examined the influence of temperature, HCl, water vapor, and H<sub>2</sub>/CO concentration on mercury oxidation.

Figure 1 summarizes the influence of water vapor on mercury oxidation. Consistent with chemical kinetic modeling, the results show that the presence of water acts to inhibit Hg oxidation. The chemical kinetics suggest that this is due to significantly lower Cl concentrations resulting from  $\text{Cl} + \text{H}_2\text{O} \rightarrow \text{HCl} + \text{OH}$ . Figure 2 shows the results of varying the amount of H<sub>2</sub> added to a chlorine-deficient system (39 ppm HCl). These results indicate a significant promotion of oxidation depending on the temperature at which the H<sub>2</sub> is added. At high temperature the H<sub>2</sub> actually inhibits oxidation, something the chemical kinetics suggest is due to

$\text{H}_2 + \text{Cl} \rightarrow \text{HCl} + \text{H}$ . This highlights the importance of selecting the proper temperature for the addition. Other tests (not shown) examine the influence of CO on the process. The results indicate that straight CO does not influence Hg oxidation, while combinations of  $\text{H}_2$  with CO lead to results that are very similar to the  $\text{H}_2$  by itself. The presence of the CO does tend to slightly increase the oxidation over that of the  $\text{H}_2$  by itself at 978 K, but yields no change at 922 or 1200 K.

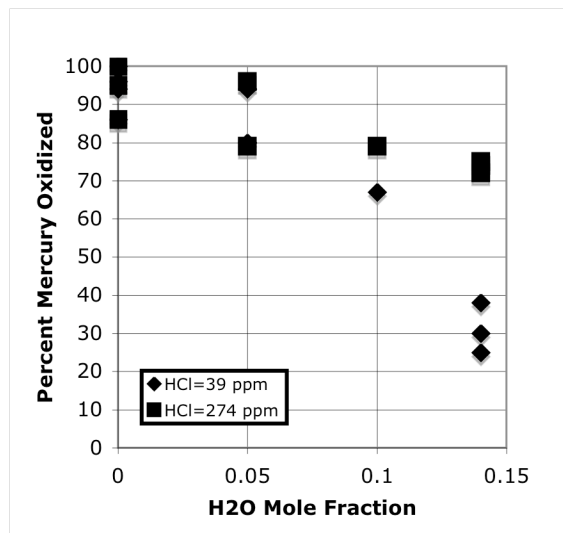


Figure 1. Influence of  $\text{H}_2\text{O}$  on Hg oxidation

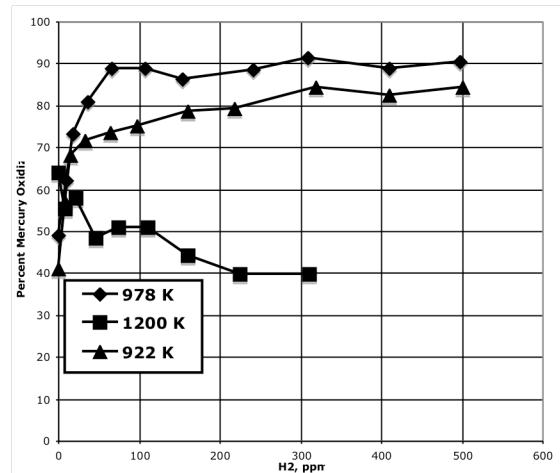


Figure 2. Influence of  $\text{H}_2$  on Hg oxidation

## FUTURE WORK

The future work is focused on finding the information needed to determine whether such a promotion system is practical, and if so, what it would look like. First, the fact that a  $\text{H}_2/\text{CO}$  mix appears effective suggests that a small natural gas steam reformer could be used to supply the fuel. Second, the data suggest that most of the effect of the promotion is achieved for fairly low  $\text{H}_2$  concentrations (<100 ppm from Figure 2), indicating a small natural gas requirement. To be useful as a potential Hg control strategy, however, the practitioner must know where to inject the secondary fuel in a non-isothermal system, and how much to inject. Our proposed work to complete this grant is designed to address these issues. First, we will complete the planned isothermal experiments. Next, we will update our chemical kinetic model using the latest literature, where there has been substantial progress over the last five years. Detailed comparison of model with data over the full range of experiments will be done to determine whether the current models are able to reasonably capture the trends. If not, our work will focus on kinetic model development. If so, we will use the validated model to study the expected behavior in non-isothermal systems. The idea is to use a quench rate similar to that in a boiler to identify the optimum injection location for a practical system. This should be followed by non-isothermal validation experiments, which would be beyond the scope of the present project.

## LIST OF PAPERS PUBLISHED, U.S. PATENT/PATENT APPLICATIONS, CONFERENCE PRESENTATIONS, AWARDS RECEIVED AS A RESULT OF SUPPORTED RESEARCH, STUDENTS SUPPORTED UNDER THIS GRANT

### Conference Presentations

- Study of the forced oxidation of mercury in post-combustion gases. L. Castiglione and J. Kramlich. Pacific Northwest Regional Environmental Symposium, 2004.

### Students Supported Under this Grant

- Linda Castiglione, Ph.D. student in the Department of Mechanical Engineering, University of Washington